# TITLE OF THE INVENTION

MAGNETIC MATERIAL

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 2001-090953, filed March 27, 2001, the entire contents of which are incorporated herein by reference.

## BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a magnetic material and, more particularly, to a magnetic material capable of realizing magnetic refrigeration using a relatively low magnetic field in near room temperature region.

2. Description of the Related Art

Presently, a gas compression/expansion cycle is primarily used in refrigeration systems, e.g., refrigerators, freezers, and air-conditioners, closely related to daily human life. However, this gas compression/expansion cycle is environmentally problematic, in terms of the exhaustion of specific freon gases. In addition, substitute freon gases presumably have a bad effect on the environment. From this background, clean and efficient refrigeration technologies causing no environmental problems due to wastage of operating gases are being demanded to put

into practical use.

Recently, magnetic refrigeration is being increasingly expected as one such environment-friendly, highly efficient refrigeration technology. Much research and development of the related technologies for use in near room temperature region has been undertaken. Magnetic refrigeration generates low temperatures as follows by applying the magnetocaloric effect (a phenomenon in which when an external magnetic field is changed with respect to a magnetic material while the magnetic material is thermally insulated, the temperature of this magnetic material changes).

The entropy of a magnetic material is changed depending on whether a magnetic field is applied or not, owing to the difference between the degrees of freedom of the electron spin system. With this entropy change, the entropy transfers between the electron spin system and the lattice system. Magnetic refrigeration uses a magnetic material having a large electron spin and produces a large entropy change between the magnetic field applied state and the magnetic field removed state. Using this large entropy change, magnetic refrigeration generates low temperatures.

Note that in a temperature region of 1 K or more, a "magnetic material" usually means a substance which shows magnetism due to an electron spin. On the other hand, in a temperature region of a few mK or less,

magnetism due to a nuclear spin becomes relatively large. For example, an ultra low temperature of 27 $\mu$K was reportedly generated by using $PrNi_5$. In the following description, a "magnetic material" means a substance showing magnetism due to an electron spin, and a target temperature region is 1 K or more, unless otherwise specified.

In the early 1900s, magnetic refrigeration systems using paramagnetic salts such as $Gd_2(SO_4)_3.8H_2O$ and paramagnetic compounds represented by $Gd_3Ga_5O_{12}$ (gadolinium gallium garnet "GGG") were developed. However, these magnetic refrigeration systems using paramagnetic materials were in most cases applied to an low temperature region of 20 K or less for the following reason. That is, as the lattice vibration increases with an increase in temperature, the higher magnetic field is required to reduce the lattice vibration by entropy transferring between electron spin system and lattice system. Therefore, assuming a magnetic field of about 10 tesla which can be obtained using an ordinary type superconducting magnet, temperatures at which magnetic refrigeration can be achieved using paramagnetic materials are limited to the low temperature region of 20 K or less.

On the other hand, to realize magnetic refrigeration at higher temperatures, the research of magnetic refrigeration using the magnetic phase

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transition of a ferromagnetic material between a
paramagnetic state and a ferromagnetic state was
extensively made after the 1970s.  As a consequence, a
large number of magnetic materials containing rare

5      earth elements having a large electron magnetic spin
per unit volume have been proposed.  Examples are
lanthanoide rare earth elements such as Pr, Nd, Dy, Er,
Tm, and Gd, rare earth alloy materials containing two
or more rare earth elements such as Gd-Y and Gd-Dy, and

10     rare earth intermetallic compounds such as $RAI_2$ (R
represents a rare earth element, and this similarly
applies to the following description), $RNi_2$, and GdPd.

When any of these ferromagnetic substances are
used, an external magnetic field is applied at a

15     temperature close to the ferromagnetic phase transition
temperature (Curie temperature; Tc), thereby causing
the magnetic phase transition of electron spin system
from a paramagnetic state to a ferromagnetic ordered
state.  Magnetic refrigeration is realized by using the

20     resulting entropy change.  Therefore, the applicable
temperature range is limited to the vicinity of the
ferromagnetic phase transition temperature (Tc) of each
magnetic material.  However, the magnitude of the
external magnetic field need only be the one enough to

25     assisting a magnetic phase transition.  A magnetic
field of this magnitude can be well generated in a
temperature region much higher than 20 K.

In 1974, Brown (U.S.A.) achieved magnetic refrigeration at room temperature for the first time, by using a ferromagnetic substance Gd plate having a ferromagnetic phase transition temperature (Tc) of

5    about 294 K. Unfortunately, although the refrigeration cycle was continuously operated in the experiment, there were some problems such as heat transfer in a refrigeration cycle, because an integral Gd plate was used in the range of the hot end to the cold end.

10    Magnetic refrigeration in the range of intermediate temperatures much higher than 20 K to room temperature has a substantial problem. That is, lattice vibration becomes large as the temperature rises, so, in a temperature region of 100 to 150 K or

15    more the lattice system entropy becomes large compared with the magnetic entropy of the electron spin system. Accordingly, even when the entropy is exchanged between the electron spin system and the lattice system by changing the magnitude of the external magnetic field,

20    the magnetocaloric effect, i.e., a temperature reduction ($\Delta$Tad) of the magnetic substance is small.

In 1982, Barclay (U.S.A.) attempted to use the lattice entropy positively that had been regarded as an interference to magnetic refrigeration in the range of

25    intermediate temperatures to room temperature (or a temperature range in which the lattice entropy is large relative to the magnetic entropy), and proposed a

method of refrigeration (US-Pat. 4,332,135) in which a
magnetic material is used, in addition to magnetic
refrigeration by the magnetocaloric effect, as the
regenerator for storing coldness generated by the
5     refrigeration.  This magnetic refrigeration method is
called AMR ("Active Magnetic Refrigeration").

        In 1997, Zimm, Gschneidner, and Pecharsky of the
U.S.A. built a prototype AMR machine using a packed
column filled with fine spherical Gd, and succeeded in
10    a continuous steady-state operation of the magnetic
refrigeration cycle at room temperature ("Advances in
Cryogenic Engineering", Vol. 43, 1998).  According to
this reference, refrigeration at about 30℃ was
accomplished by changing the magnitude of the external
15    magnetic field from 0 to 5 tesla by using a
superconducting magnet at room temperature.  When the
refrigerating temperature difference ($\triangle$T) between the
hot end and the cold end was 13℃, a very high
refrigeration efficiency (COP = 15; excluding the power
20    input to the magnetic field generating means) was
reportedly obtained.  Note that the refrigeration
efficiency (COP) of a gas compression/expansion cycle
(e.g., a household refrigerator) using conventional
freon is about 1 to 3.

25        In addition to the above-mentioned technical
demonstration of the AMR-cycle magnetic refrigeration
system using Gd, Pecharsky and Gschneidner of the

U.S.A. developed a $Gd_5(Ge,Si)_4$-based material as a magnetic material from which a very large entropy change can be obtained at room temperature (US-Pat. 5,743,095). For example, $Gd_5(Ge_{0.5}Si_{0.5})_4$ shows an entropy change ($\Delta S$) of about 20 J/(kg·K) when the magnitude of the external magnetic field is changed from 0 to 5 tesla at about 277 K, and shows an entropy change ($\Delta S$) of about 15 J/(kg·K) when the magnitude of the external magnetic field is changed from 0 to 2 tesla. That is, a large entropy change twice or more that of Gd is observed near room temperature.

Unfortunately, in the experiments conducted by Zimm, Gschneidner, and Pecharsky described above, a superconducting magnet was used to apply a large external magnetic field of about 2 to 5 tesla to Gd as a magnetic material for magnetic refrigeration. Since under the present conditions a cryogenic environment at about 10 K is necessary to operate a superconducting magnet, the system increases in size. In addition, when a superconducting magnet is to be used, it is necessary to use a freezing medium such as liquid helium or a refrigerator for cryogenic generation. It is impractical to apply a system like this to ordinary purposes such as refrigeration and air-conditioning.

A heavy duty electromagnet is another means for generating a large magnetic field, other than a superconducting magnet. When this electromagnet is to

be used, however, a large input current and water
cooling against Joule heating are necessary.  This
makes the system larger and also increases the
operation cost.  Accordingly, similar to the case of a

5    superconducting magnet, it is impractical to apply a
system using an electromagnet for usual purposes.

A permanent magnet is a small convenient magnetic
field generating means.  However, it is difficult to
generate a large magnetic field of about 2 to 5 tesla

10   using such a magnet.  According to the reported results
of experiments using an NdFeB-based permanent magnet
and Gd as a magnetic material for magnetic
refrigeration, the cooling temperature at room
temperature is very low, 1.6℃, because the magnitude of

15   the magnetic field is small.  This greatly differs from
the refrigerating ability of the conventional gas
compression/expansion cycle.

BRIEF SUMMARY OF THE INVENTION

The present invention has been made in considera-

20   tion of the problems of the magnetic refrigeration
technologies in near room temperature region.  It is an
object of the present invention to provide a magnetic
material for magnetic refrigeration, by which magnetic
refrigeration can be realized using a relatively low

25   magnetic field.

The magnetic material of the present invention is
characterized by exhibiting, in a certain temperature

region (only in a partial temperature region), an inflection point at which a second order differential coefficient of a magnetization curve changes from positive to negative with respect to a magnetic field,

5    within the range of the strength of the magnetic field obtained using a permanent magnet.

Preferably, the magnetic material of the present invention is characterized by exhibiting, only in part of the temperature region from 200 K to 350 K, the

10   above-mentioned inflection point on a magnetization curve within the range of the strength of a magnetic field of 1 tesla or less.

In the present invention, an external magnetic field is applied using a permanent magnet unit, near a

15   temperature indicating the inflection point, to a magnetic material having a magnetization curve meeting the above condition.  Magnetic refrigeration can be realized by transferring entropy between the electron spin system and the lattice system by changing the

20   magnitude of the external magnetic field.

The inventors of the present application found that within the range of near room temperature from 200 K to 350 K (i.e., temperatures closely related to everyday life, e.g., from the temperature of dry ice to

25   that of hot water), and within the range of the strength of a relatively low magnetic field of 1 tesla or less, it is effective to urge a ferromagnetic

interaction and an antiferromagnetic interaction to compete with each other, as a means for obtaining the inflection point as described above on a magnetization curve.

5    The reason why the above-mentioned inflection point appears on a magnetization curve is presumably as follows. By urging a ferromagnetic interaction and an antiferromagnetic interaction to compete with each other, several electronic states having close energy

10    levels are formed. The relation of the energy levels of each electronic states changes in accordance with the amplitude of the external magnetic field. Hence, upon application of a magnetic field, the magnetic spin configuration partly or entirely changes inside the

15    material system. As a consequence, the inflection point appears on a magnetization curve.

The important point is that in near room temperature region from 200 K to 350 K, several electronic state is in very close energy level. A

20    large entropy change cannot be obtained, i.e., efficient magnetic refrigeration cannot be realized by the application of a relatively low magnetic field, unless this special condition is formed.

In addition, when magnetic refrigeration is

25    actually performed using a magnetic material, not only the magnitude of an entropy change $\Delta S(T, \Delta H)$ corresponding to a magnetic field change ($\Delta H$), but

also a temperature range with which the peak of the

entropy change appears is an important factor. That

is, even when a large entropy change is obtained, if

this entropy change is obtained only within a very

5    narrow temperature range (e.g., about 1 to 2 K), the

magnetic refrigeration cycle cannot be stably operated.

More specifically, a stable refrigeration cycle cannot

be achieved, or even if it can be achieved, is

impractical for use in a refrigerator.

10        In the case of the AMR, for example, a magnetic

material works as not only the magnetic refrigerant but

also the regenerator, so a temperature gradient is

generated inside a magnetic refrigeration chamber when

the refrigeration cycle is operated in a steady state.

15    That is, even when the temperature of the magnetic

material is almost uniform in the magnetic

refrigeration chamber at the beginning of the

operation, a temperature gradient is gradually formed

in the magnetic refrigeration chamber as the

20    refrigeration cycle is repeated. This makes the two

end portions of the magnetic refrigeration chamber

become hot and cold ends. Consequently, the magnetic

material in the magnetic refrigeration chamber operates

at temperature cycles of different ranges at different

25    positions. In a steady-state operation, these

temperature cycles are also in a steady state. If the

magnetic material is the one with which the peak of an

entropy change appears only within a very narrow
temperature range (e.g., 1 to 2 K), a refrigeration
cycle is achieved only within this narrow temperature
range. Accordingly, it is difficult to perform stable
operation in a large refrigeration temperature
difference (e.g., 10 K to 20 K or a larger range) using
such a material.

Note that it is also possible to arrange magnetic
materials exhibiting the peak of an entropy change in
different temperature regions, in accordance with this
temperature gradient during a steady-state operation,
from the hot end to the cold end of the magnetic
refrigeration chamber. However, the steady state is
gradually approached through different temperature
cycles as the refrigeration cycle is repeated from the
start of operation. Therefore, each magnetic material
must be a substance by which an entropy change appears
within a temperature range wider than the temperature
amplitude during steady-state operation.

For the reasons described above, a magnetic
material for magnetic refrigeration must have a large
entropy change and a wide temperature range (width)
over which a peak appears in an entropy change. Note
that the temperature width of the peak of an entropy
change means the bottom width of the peak, not the
half-width. This is so because the effective
temperature width of the peak has an effect in an

actual temperature cycle. This effective temperature width of the peak is a peak width obtained by removing an error level from the bottom portion.

Letting $\Delta S(T, \Delta H)$ be an entropy change (temperature dependence) at a temperature T with respect to a specific external magnetic field change $\Delta H$ and $\Delta Smax$ be the peak value of $\Delta S$, the effective temperature width of the peak is defined as follows: the range of the temperature T within which $\Delta S(T, \Delta H) > 0.1 * \Delta Smax$, when a value which is 1/10 of $\Delta Smax$ is a bottom level reference, or, if $0.1 * \Delta Smax > 1$ [J/(kg,K)] is met, the range of the temperature T within which $\Delta S(T, \Delta H) > 1$ [J/(kg,K)], regarding 1 [J/(kg,K)] as a bottom level reference.

To realize a magnetic refrigeration cycle by using a single magnetic material, the effective temperature width of the peak of the entropy change $\Delta S(T, \Delta H)$ must be 3 K or more. This effective temperature width is preferably about 5 K or more, and more preferably, 8 K or more.

Additionally, the peak of the entropy change described above preferably has no temperature hysteresis. Even if the peak has a temperature hysteresis, this hysteresis is 8 K or less, preferably, 3 K or less, and more preferably, 1 K or less.

However, the research to-date reveal that an entropy change and the temperature width of its peak

often have a tradeoff relationship. Therefore, it is
important to obtain a good balance between them.

If the peak width of an entropy change is as
narrow as about 1 to 2 K, giving a slight composition
5    fluctuation is effective as a means for widening the
peak width so that the peak width becomes a practical
one. By giving this slight composition fluctuation, it
is possible to slightly change the energy level balance
of electronic state in microscopic portions, without
10   largely changing the physical characteristics of a
magnetic material, and to distribute a temperature at
which the inflection point appears within a microscopic
region. As a consequence, the peak width of an entropy
change in a magnetic material can be increased.

15   When the metal texture is taken into
consideration, the peak width of an entropy change can
also be increased, without largely changing the
physical characteristics of a magnetic material as
described above, by precipitating a small amount of a
20   second phase, having a crystal structure different from
that of a main phase, with respect to this main phase.
Practically no problem arises if the amount of this
second phase is 30 vol% or less. This can increase the
peak width of $\Delta S$.

25   Examples of practical methods are to use a
preparation composition slightly different from a
predetermined composition, slightly add additional

elements, and rapidly cool a metal in a molten state during synthesis.

To obtain a large entropy change, the internal system of magnetic material must have large degree of freedom. To increase the degree of freedom of internal magnetic system of a magnetic material, it is preferable to use transition metal elements such as Fe, Ni, Co, Mn, and Cr, or rare earth elements such as Pr, Nd, Gd, Tb, Dy, Er, Ho, or Tm, as main constituent elements.

Furthermore, to obtain the inflection point as described above on a magnetization curve within the range of a magnetic field of 1 tesla or less in near room temperature region of about 200 K to about 350 K, it is effective to add a total of 50 atomic % or more of one or more of Fe, Ni, Co, Mn, and Cr. This is so because, if the ratio of a transition metal element such as Fe is low, it becomes difficult to make the above inflection point appear in a high-temperature region of 200 K or more with a magnetic field of 1 tesla or less.

When Gd, Sm, or Tb having a relatively strong magnetic interaction among other rare earth elements is used, the total amount of this element and a transition metal element such as Fe, Co, Ni, Mn, or Cr enumerated above is preferably 60 atomic % or more, in order to make the above inflection point appear at a temperature

of 200 K or more.

A magnetic material meeting the above condition
is, e.g., a magnetic material which comprises

a total of 50 to 96 atomic % of one element or two
or more elements selected from the group consisting of
Fe, Co, Ni, Mn, and Cr,

a total of 4 to 43 atomic % of one element or two
or more elements selected from the group consisting of
Si, C, Ge, Al, B, Ga, and In, and

a total of 4 to 20 atomic % of one element or two
or more elements selected from the group consisting
of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,
and Yb.

In the second group, Si or Ge is preferred, and 4
to 25 atomic % of Si are particularly preferred.

Representative examples of this magnetic material
are $R(T,M)_{13}$, $R(T,M)_{12}$, $R_2(T,M)_{17}$, and $R_3(T,M)_{29}$ (R is
a rare earth element, T is a transition element, and M
is the above element of group 3B or 4B).  This magnetic
material is particularly preferably
$(La,Pr,Ce,Nd)(Fe,T,Si)_{13}$ or $(La,Pr,Ce,Nd)(Fe,T,Si,M)_{13}$.

Another magnetic material meeting the above
condition is, e.g., a magnetic material which comprises

a total of 60 to 96 atomic % of one element or two
or more elements selected from the group consisting of
Fe, Co, Ni, Mn, and Cr, and

a total of 4 to 40 atomic % of one element or two

or more elements selected from the group consisting of Sc, Ti, Y, Zr, Nb, Mo, Hf, Ta, and W. Note that two or more elements are particularly preferably selected from the second group.

5    In this second group, Ti, Zr, Nb, and Hf are particularly favorable, and their total amount is preferably 25 atomic % or more.

A representative example of this magnetic material is $(Hf,Ta)Fe_2$, $(Ti,Sc)Fe_2$, and $(Nb,Mo)Fe_2$.

10    From a viewpoint of practical use, a magnetic material for magnetic refrigeration should better exhibit large change in magnetic entropy per weight or per volume to minimize the weight and volume of refrigeration systems. In addition, from another

15    viewpoint of practical use, it should preferably exhibit large change in magnetic entropy per unit magnetic moment. The reason is as follows. In the gradient of magnetic field, a magnetic material is affected by external force (magnetic force) which is proportional to

20    the magnetic moment of the material. The magnetic force is one of the disturbance factors in practical use when the relative position between the magnetic material and the permanent magnet is controlled.

A magnetic material meeting the above condition is,

25    e.g., a magnetic material which comprises

a total of 50 to 80 atomic % of one or not less than two elements selected from the group consisting of

Fe, Co, Ni, Mn, and Cr,

a total of 20 to 50 atomic % of one or not less than two elements selected from the group consisting of Sb, Bi, P, and As.

Representative examples of this magnetic material are $(Mn,Cr)_2(Sb,As,P)$, $(Mn,Cr)(Sb,As,P,Bi)$, $(Co,Mn,Fe,Ni)_2(P,As)$, and $(Fe,Co,Mn)_3P$. This magnetic material is particularly preferably $(Mn,Cr)_2Sb$, $(Mn,Cr)Sb$, $(Co,Mn)_2P$, and $(Fe,T)_2(P,As)$.

To control the electronic state subtly, it is effective to substitute a part (below 10 %) of 3B transition element such as Fe, Co, Ni, Mn or Cr with 4B transition element such as Rh or Pd. In addition, a part (below 20 %) of 5B transition element such as Sb, Bi, P and As is substituted for light element such as B or C, to control the electronic state subtly.

If the content of oxygen is large in the manufacture of the above magnetic material, this oxygen and a metal element combine to form a refractory oxide in a melting step (of melting and mixing materials). This oxide floats as a refractory impurity in the molten metal layer, and reduces the quality of the material manufactured in the melting step and resolidification step. To minimize the formation of this oxide, therefore, the oxygen content is preferably decreased to 1 atomic % or less.

In the magnetic material of the present invention,

the inflection point as described above appears within the range of a relatively low magnetic field. Accordingly, a magnetic refrigeration system can be realized by using a small permanent magnet unit,

5    without using any superconducting magnet or electromagnet having a large current capacitance, near a temperature at which the inflection point appears.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a graph showing examples of the

10    magnetization curves of a magnetic material (specimen 1) based on the present invention;

FIG. 2 is a graph showing examples of the magnetization curves of a magnetic material (specimen 4) based on the present invention;

15    FIG. 3 is a graph showing examples of the magnetization curves of a magnetic material (specimen 6) used as a comparative example;

FIG. 4 shows the temperature dependency of the entropy change of the magnetic material (specimen 1)

20    based on the present invention;

FIG. 5 is a graph showing examples of the magnetization curves of a magnetic material (specimen 11) based on the present invention;

FIG. 6 is a graph showing examples of the

25    magnetization curves of a magnetic material (specimen 13) used as a comparative example;

FIG. 7 is a graph showing examples of the

magnetization curves of a magnetic material (specimen 21) base on the present invention;

FIG. 8 is a schematic perspective view showing the arrangement of a magnetic refrigeration system using the magnetic material based on the present invention; and

FIG. 9 is a schematic view showing the arrangement of a heat exchange medium circulating system in the magnetic refrigeration system using the magnetic material of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Several examples of a magnetic material based on the present invention will be explained below.

(Example 1)

Seven types of magnetic materials having the following compositions were manufactured, and these materials were tested for their magnetization curves and entropy changes due to the change in external magnetic field. In the following specimens, specimens 1 to 4 are magnetic materials based on the present invention, and specimens 5, 6, and 7 are comparative examples.

Specimen 1: $Fe_{81.7}Si_{11.1}La_{7.2}$

Specimen 2: $Fe_{80.8}Si_{12.1}La_{7.1}$

Specimen 3: $Fe_{82.6}Co_{0.9}Si_{9.3}La_{7.2}$

Specimen 4: $Fe_{81.7}Si_{10.2}Ga_{0.9}La_{7.2}$

Specimen 5: $Fe_{69.7}Al_{23.2}La_{7.1}$

Specimen 6: $Fe_{75.8}Si_{17.1}La_{7.1}$

Specimen 7: $Gd_{95}Y_5$

After these materials having the above

composititons were adjusted by arc melting, they were

5    subjected to uniformization annealing in a vacuum at a

temperature of 900°C to 1,100°C for two weeks.  These

specimens thus manufactured were tested for their

magnetization curves.

FIG. 1 shows the magnetization curves of specimen

10    1 at temperatures of 157.5 K to 232.5 K.  FIG. 2 shows

the magnetization curves of specimen 4 at temperatures

of 192.5 K to 217.5 K.  FIG. 3 shows the magnetization

curves of specimen 6 at temperatures of 200 K to 270 K.

The magnetization curves of specimen 1 (FIG. 1)

15    indicate that the magnetic moment abruptly increased by

a relatively low external magnetic field in a

temperature region lower than T = 196.5 K, and, within

the range of a magnetic field of 1 tesla or less, a

second order differential coefficient of the magnetic

20    moment was negative with respect to the magnetic field

(upward convex shape) (symbols a to d in FIG. 1).

The shape of this magnetization curve largely

changed near T = 200 K.  When T = 200.5 K (symbol e)

and 202.5 K (symbol f), the value of the magnetic

25    moment was small with respect to a very low magnetic

field of about 0.01 tesla.  As the magnetic field

increased, however, the magnetic moment abruptly

increased near the magnetic field $H = 0.35$ tesla and $H = 0.6$ tesla, and an inflection point appeared on the magnetization curve. After passing through this inflection point, the increase in the magnetic moment reduced. The value of the magnetic field when this inflection point appeared on the magnetization curve will be represented by Hc hereinafter.

As the temperature was further raised, Hc increased, and the change in the magnetic moment near Hc reduced. When the temperature was higher than $T = 207.5$ K (symbol g), the range of the magnetic field within which the magnetic moment increased near Hc broadened and gradually disappeared (symbols h to k in FIG. 1).

The magnetization curves of specimen 4 (FIG. 2) show that the magnetic moment abruptly increased by a relatively low external magnetic field in a temperature region lower than $T = 202.5$ K, and, within the range of a magnetic field of 1 tesla or less, a second order differential coefficient of the magnetic moment with respect to the magnetic field was negative (upward convex shape) (symbols a to c in FIG. 2).

The shape of this magnetization curve largely changed near $T = 207.5$ K. When $T = 207.5$ K (symbol d), the magnetization curve exhibited concave shape (the second order differential coefficient was positive) near the magnetic field $H = 0.3$ tesla to $H = 0.4$ tesla.

The magnetization curve turned to a upward convex shape when the magnetic field H = 0.5 tesla or more. That is, an inflection point appeared on the magnetization curve near the magnetic field H = 0.45 tesla.

5    Note that similar magnetization curves were observed for specimens 2 and 3: an inflection point appeared within the range of a magnetic field of 1 tesla or less near T = 207 K for specimen 2 and T = 230 K for specimen 3.

10   In contrast, the magnetization curves of specimen 6 (FIG. 3) reveal that the value of the magnetic moment largely changed near the magnetic phase transition temperature, but, within the range of a magnetic field of 1 tesla or less, a second order differential

15   coefficient of the magnetic moment with respect to this magnetic field was always negative, so there was no large change in the shape (upward convex shape) of the magnetization curve. Note that similar magnetization curves were observed for specimens 5 and 7: within the

20   range of a magnetic field of 1 tesla or less, a second order differential coefficient of the magnetic moment with respect to this magnetic field was always negative.

For each of these seven specimens, an entropy

25   change $\Delta S(T, \Delta H)$ of the electron spin system due to the change in external magnetic field was calculated from magnetization measurement data by using the following

equation. In each specimen, a peak appeared in the entropy change $\Delta S$ at a specific temperature (Tpeak) with respect to a change $\Delta H$ of an arbitrary magnetic field.

5

$$\Delta S(T, \Delta H) = \int_0^{\Delta H} \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH$$

FIG. 4 shows the entropy change of specimen 1 as a function of the temperature. As shown in FIG. 4, when the magnetic field strength was changed from 0 to

10    0.5 tesla or from 0 to 1 tesla, a peak appeared in the entropy change at a temperature between about 195 K and about 210 K.

Table 1 shows the calculation result of an entropy change ($\Delta$ Smax) with respect to the change in magnetic

15    field strength $\Delta H$ at Tpeak (the temperature at which a peak appeared in the entropy change), for each of the specimens. For comparison, Table 1 also shows the entropy change of the electron spin system of Gd as a prototype of a magnetic material for magnetic

20    refrigeration.

Table 1   Entropy change : $\Delta S_{max}[J/(K \cdot Kg)]$

| Change in magnetic field strength $\Delta H$[tesla] | Specimen No. | | | | | | | Remarks Gd |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| 0 – 0.1 | 1.7 | 1.6 | 0.9 | 1.3 | 0.21 | 0.23 | 0.34 | 0.43 |
| 0 – 0.2 | 4.6 | 3.2 | 1.8 | 2.5 | 0.41 | 0.45 | 0.72 | 0.87 |
| 0 – 0.3 | 8.2 | 5.1 | 2.7 | 3.7 | 0.64 | 0.66 | 1.07 | |
| 0 – 0.4 | 10.7 | 6.9 | 3.8 | 4.8 | 0.83 | 0.89 | 1.4 | 1.6 |
| 0 – 0.5 | 12.1 | 8.3 | 4.6 | 5.8 | 1.04 | 1.1 | 1.7 | |
| 0 – 0.6 | 13.1 | 9.6 | 5.4 | 6.5 | 1.2 | 1.3 | 2.0 | 2.2 |
| 0 – 0.8 | 14.5 | 11.5 | 6.6 | 7.6 | 1.4 | 1.6 | 2.5 | 2.7 |
| 0 – 1.0 | 15.2 | 12.6 | 7.4 | 8.4 | 1.6 | 1.8 | 3.0 | 3.2 |
| $T_{peak}$(K) | 200 | 207 | 230 | 205 | 250 | 240 | 285 | 295 |

$\Delta S_{max} = \Delta S(T_{peak}, \Delta H)$

$T_{peak}$: the temperature at which a peak is observed in the temperature dependency of the entropy change

As can be seen from Table 1, large entropy changes were observed for a low magnetic field of 1 tesla or less in specimens 1 to 4, indicating that these specimens were much superior to Gd. In contrast, entropy changes measured in specimens 5 to 7 were equivalent to or smaller than Gd, showing that these specimens 5 to 7 were largely inferior to specimens 1 to 4.

As described previously, when magnetic refrigeration is actually performed using a magnetic material, not only the magnitude of the entropy change $\Delta S(T, \Delta H)$ due to the change ($\Delta H$) in the magnetic field, but also a temperature width ("effective temperature width") by which a peak appears in the entropy change is an important factor. As numerical value for comparison, the temperature widths of the individual specimens for $\Delta S(T, \Delta H = 1 \text{ tesla})$ and $\Delta S(T, \Delta H = 0.5 \text{ tesla})$ are presented below.

When the change in magnetic field strength $\Delta H$ is 1 tesla, the temperature widths of the peaks of the entropy changes of specimens 1 to 4 are as follows:

Specimen 1: approximately 190 to 210 K

Specimen 2: approximately 195 to 220 K

Specimen 3: approximately 215 to 245 K

Specimen 4: approximately 195 to 217 K

When the change in magnetic field strength $\Delta H$ is 0.5 tesla, the temperature widths of the peaks of the

entropy changes of specimens 1 to 4 are as follows:

Specimen 1: approximately 194 to 207 K

Specimen 2: approximately 197 to 218 K

Specimen 3: approximately 220 to 237 K

5      Specimen 4: approximately 196 to 218 K

As described above, even when the change in magnetic field strength $\Delta H$ is 0.5 tesla, each of specimens 1 to 4 has a temperature width of 10 K or more and hence has no problem in practice.

10      In each of specimens 1 to 4 as mentioned above, when the temperature was higher than a characteristic temperature (Tcri), the state of electron spin configurations greatly changed by a relatively low magnetic field of 1 tesla or less, and the inflection

15      point appeared on the magnetization curve. In addition, in each of theses specimens, an extremely large entropy change was observed in the electron spin system near the temperature at which the inflection point appeared on the magnetization curve.

20      Note that X-ray diffraction revealed that in each of specimens 1 to 4, the main phase was a cubic crystal structure, and an $\alpha$ Fe phase slightly precipitated as the second phase.

(Example 2)

25      Three types of magnetic materials having the following compositions were manufactured, and these materials were tested for their magnetization curves

and entropy changes due to magnetic field changes. In the following specimens, specimens 11 and 12 are magnetic materials based on the present invention, and specimen 13 is a comparative example.

Specimen 11: $Fe_{67}Hf_{28}Ta_5$

Specimen 12: $Fe_{67}Hf_{27}Ta_6$

Specimen 13: $Fe_{67}Hf_{29}Ta_4$

After these materials having the above compositions were adjusted by arc melting, they were subjected to uniformization annealing in a vacuum at a temperature of 950°C to 1,000°C for about 100 hr, thereby manufacturing base alloys. From these base alloys, granular specimens were manufactured by using a plasma spray process. As a consequence, a large number of sphere particles having a long diameter of about 0.1 mm to about 0.3 mm were obtained. These specimens thus manufactured were tested for their magnetization curves.

FIG. 5 shows the magnetization curves of specimen 11 at temperatures of 237.5 K to 307.5K. FIG. 6 shows the magnetization curves of specimen 13 at temperatures of 277.5 K to 332.5 K.

The magnetization curves of specimen 11 (FIG. 5) indicate that the magnetic moment abruptly increased by a relatively low external magnetic field in a temperature region lower than T = 277.5 K, and, within the range of a magnetic field of 1 tesla or less, a

second order differential coefficient of the magnetic
moment with respect to the magnetic field was negative
(upward convex shape) (symbols a to e in FIG. 5).

The shape of this magnetization curve largely

5     changed near T = 280 K.  When T = 280.5 K (symbol f)
and 282.5 K (symbol g), the value of the magnetic
moment was small with respect to a very low magnetic
field of about 0.01 tesla.  As the magnetic field
increased, however, the magnetic moment abruptly

10    increased near the magnetic field H = 0.27 tesla and
H = 0.5 tesla, and an inflection point appeared on the
magnetization curve.  After passing through this
inflection point, the increase in the magnetic moment
reduced.

15    As the temperature was further raised as in the
case of specimen 1 in Example 1, the value of Hc (the
magnetic field with which an inflection point appears
on the magnetization curve) increased, and the change
in the magnetic moment near Hc reduced.  When the

20    temperature was higher than T = 292.5 K (symbol j),
the transition near Hc gradually disappeared (symbols j
to l).

Note that similar magnetization curves were
observed for specimen 12: near T = 245 K, an inflection

25    point appeared on the magnetization curve in a magnetic
field of 1 tesla or less.

In contrast, similar to specimen 6 (comparative

example) in Example 1, the magnetization curves of specimen 13 (FIG. 6) reveal that the value of the magnetic moment largely changed near the magnetic phase transition temperature, but, within the range of a

5    magnetic field of 1 tesla or less, a second order differential coefficient of the magnetic moment was always negative with respect to this magnetic field, so there was no large change in the shape (upward convex shape) of the magnetization curve.

10    For each of these three specimens, an entropy change $\Delta S(T, \Delta H)$ of the electron spin system due to the change in external magnetic field was evaluated in the same manner as in Example 1. Table 2 shows the calculation result of an entropy change ($\Delta S_{max}$) with

15    respect to the change in magnetic field strength $\Delta H$ at Tpeak (the temperature at which a peak appeared in the entropy change), for each of the specimens.

Table 2    Entropy change : $\Delta S_{max}[mJ/(K \cdot cm^3)]$

| Change in magnetic field strength $\Delta H$[tesla] | Specimen No. | | | Remarks Gd |
|---|---|---|---|---|
| | 11 | 12 | 13 | |
| 0 - 0.1 | 3.6 | 4.2 | 1.3 | 3.4 |
| 0 - 0.2 | 8.9 | 11.1 | 2.9 | 6.8 |
| 0 - 0.3 | 14.4 | 16.8 | 4.5 | |
| 0 - 0.4 | 19.4 | 21.2 | 6.0 | 12.6 |
| 0 - 0.5 | 24.0 | 24.9 | 7.4 | |
| 0 - 0.6 | 27.1 | 28.1 | 8.9 | 17.5 |
| 0 - 0.8 | 30.8 | 30.8 | 11.5 | 21.7 |
| 0 - 1.0 | 35.2 | 32.7 | 14.4 | 25.7 |
| $T_{peak}$(K) | 282 | 245 | 315 | 295 |

$\Delta S_{max} = \Delta S(T_{peak}, \Delta H)$
$T_{peak}$:the temperature at which a peak is
observed in the temperature dependency
of the entropy change

As can be seen from Table 2, large entropy changes
were observed for a low magnetic field of 1 tesla or
less in specimens 11 and 12, indicating that these
specimens were much superior to specimen 13.

Furthermore, results analogous to those of
specimens 12 and 13 described above were obtained for
an Fe-T-Sc-based magnetic material containing about
67 atomic % of Fe and about 25 to 30 atomic % of Ti.
(Example 3)

Two types of magnetic materials having the
following compositions were manufactured, and these
materials were tested for their magnetization curves
and entropy changes due to the change in external
magnetic field.

Specimen 21: $Mn_{63.4}Cr_{3.3}Sb_{33.3}$

- 32 -

Specimen 22: $Mn_{50}As_{35}Sb_{15}$

The raw materials in powdery form having the above compositions were mixed, sealed in a crucible, and kept at a temperature of 800℃ to 950℃, generating chemical
5      reaction slowly for a long period (about 2 days for specimen 21, about 1 week for specimen 22). Specimen 21 and 22 were subjected to uniformization annealing in a vacuum at a temperature of 550℃ to 700℃ for about 100 hr. These specimens thus manufactured were tested
10     for their magnetization curves.

FIG. 7 shows the magnetization curves of specimen 21 at temperatures of 300 K to 315 K. The magnetization curves of specimen 21 at temperature of 315 k indicated that, within the range of magnetic
15     field of 1 tesla or less, a second order differential coefficient of the magnetic moment was always negative with respect to the magnetic field (upward convex shape) (symbols g in FIG. 7).

In the case of specimen 21, on the contrary to
20     specimen 1 and 11, as the temperature was lowered, concave shape appeared in the magnetization curve.

When T = 310 K (symbol c), within the range of magnetic field of 0.4 tesla or less, the magnetization curve exhibited upward convex shape. An inflection
25     point appeared on the curve at magnetic field of near 0.4 tesla, and within the range of magnetic field from about 0.4 tesla to 0.8 tesla, the magnetization curve

exhibited concave shape. As magnetic field strength increased further, another inflection point appeared on the curve at magnetic field of near 0.8 tesla, and within the range of magnetic field of about 0.9 tesla or

5 above, the magnetization curve exhibited upward convex shape again.

As the temperature was lowered, the point at which the magnetization curve turns from concave shape to upward convex shape shifted to higher magnetic field

10 strength. For the temperature of 307.5 K, 305 K, 302.5 K and 300 K (symbols d to g), the inflection point was observed on the curve at the magnetic field strength of approximately 1 tesla, 2 tesla, 2.6 tesla and 3.5 tesla, respectively.

15 In the case of specimen 22, the result was as follows. When T = 232.5 K, an inflection point was observed on the magnetization curve at magnetic field of near 0.8 tesla, within the range of magnetic field of about 0.8 tesla or less, the magnetization curve

20 exhibited concave shape, and within the range of magnetic field of 0.8 tesla or above, the magnetization curve exhibited upward convex shape.

In the case of specimen 22, within the range of temperature from 200 K to 230 K, and within the range of

25 magnetic field of 1.0 tesla or less, the magnetization curve exhibited upward convex shape.

As the temperature was raised, when T = 232.5, as

described above, the magnetization curve turned from concave shape to upward convex shape. As the temperature was raised further, the inflection point on the curve shifts to higher magnetic field strength, and when T = 240 K, the inflection point was observed on the curve at the magnetic field of 3.8 tesla.

For specimen 21 and 22, an entropy change $\Delta S(T, \Delta H)$ of the electron spin system due to the change in external magnetic field was evaluated in the same manner as in Example 1. For specimen 21 and 22, when the magnetic field strength increased from 0 tesla to 1 tesla, the peak in the entropy change was observed at near 311 K and 231 K respectively.

Table 3 shows the calculation result of an entropy change ($\Delta S$max) per unit magnetic moment with respect to the change in magnetic field strength $\Delta H$ at Tpeak (the temperature at which a peak was observed in the entropy change), for each of the specimens.

Table 3

Entropy change : $\Delta S_{max}$ [×$10^{-3}$ mJ/(K·emu)]

| Change in magnetic field strength $\Delta H$[tesla] | Specimen No. | | Remarks Gd |
|---|---|---|---|
| | 21 | 22 | |
| 0 − 0.1 | 1.1 | 1.2 | 1.2 |
| 0 − 0.2 | 2.6 | 2.6 | 1.8 |
| 0 − 0.3 | 4.6 | 4.3 | |
| 0 − 0.4 | 6.8 | 6.0 | 2.7 |
| 0 − 0.5 | 9.0 | 7.4 | |
| 0 − 0.6 | 10.6 | 8.8 | 3.3 |
| 0 − 0.8 | 12.3 | 11.3 | 3.8 |
| 0 − 1.0 | 12.6 | 13.4 | 3.2 |
| $T_{peak}$(K) | 311 | 229 | 295 |

$\Delta S_{max} = \Delta S(T_{peak}, \Delta H)$

$T_{peak}$: the temperature at which a peak is observed in the temperature dependency of the entropy change

As can be seen from Table 3, large entropy changes per unit magnetic moment were observed for a low magnetic field of 1 tesla or less in specimens 21 and 22, indicating that these specimens were much superior to Gd.

As described previously, when magnetic refrigeration is actually performed using a magnetic material, a temperature width ("effective temperature width") by which a peak appears in the entropy change is an important factor. As numerical value for comparison, the temperature widths of the individual specimens for $\Delta S(T, \Delta H = 1$ tesla) and $\Delta S(T, \Delta H = 0.5$ tesla) are presented below.

Specimen 21: approximately 304 to 315 K

Specimen 22: approximately 214 to 236 K

When the change in magnetic field strength $\Delta H$ is

0.5 tesla, the temperature widths of the peaks of the

entropy changes of specimens 21 and 22 are as follows:

5    Specimen 21: approximately 305 to 316 K

Specimen 22: approximately 215 to 235 K

As described above, even when the change in

magnetic field strength $\Delta H$ is 0.5 tesla, each of

specimens 21 and 22 has a temperature width of 10 K or

10   more and hence has no problem in practice.


(Arrangement of magnetic refrigeration system)

A magnetic refrigeration system using the magnetic

material based on the present invention comprises a

15   magnetic refrigeration chamber, inlet pipe, outlet

pipe, and permanent magnet, as main constituent

elements.  The magnetic material is packed into the

magnetic refrigeration chamber.  A heat exchange medium

is supplied into the magnetic refrigeration chamber

20   through the inlet pipe and discharged through the

outlet pipe.  The permanent magnet is placed near the

magnetic refrigeration chamber.  By changing the

position of this permanent magnet relative to the

magnetic refrigeration chamber, a magnetic field is

25   applied to and removed from the magnetic material.  The

heat exchange medium is cooled by heat exchanging with

the magnetic material which is cooled when the magnetic

field is removed.

Preferably, the outlet pipe is divided into two piping systems. The first output pipe is used to extract, from the magnetic refrigeration chamber, the heat exchange medium used in pre-cooling of the interior of the magnetic refrigeration chamber. The second output pipe is used to extract, from the magnetic refrigeration chamber, the heat exchange medium cooled inside the magnetic refrigeration chamber. A driving unit is used to change the position of the permanent magnet relative to the magnetic refrigeration chamber. The permanent magnet is attached to this driving unit. In synchronism with a change in the relative position of this permanent magnet, the heat exchange medium outlet path from the magnetic refrigeration chamber is switched between the first and second outlet pipes, thereby forming a magnetic refrigeration cycle.

Preferably, the magnetic material is packed with a volume packing ratio of 50% to 75% into the magnetic refrigeration chamber.

In the above magnetic refrigeration system, the magnetic material is packed into the magnetic refrigeration chamber such that a space serving as a heat exchange medium passage is secured. If the packing ratio of the magnetic material in the magnetic refrigeration chamber is low, the magnetic material is

stirred by the flow of the heat exchange medium when heat is exchanged between the magnetic material and the heat exchange medium, and these two materials collide into each other. This collision cracks the magnetic material and eventually crushes the magnetic material into fine particles. Fine particles produced by the crush of the magnetic material increases the pressure loss of the heat exchange medium and lowers the refrigeration capability. In the worst case, part of the pipe clogs with the fine particles, interfering with the flow of the heat exchange medium. To avoid this, therefore, the magnetic material is packed into the magnetic refrigeration chamber with a volume packing ratio of preferably 50% to 75%, and more preferably, 60% to 70%.

Preferably, the aforementioned magnetic material consists of particles which have a particle size (long diameter) of 0.1 to 1.5 mm, and in which 87 wt% or more of the particles have an aspect ratio of 2 or less.

To realize a high refrigeration capability, it is important that heat exchange between the magnetic material packed into the magnetic refrigeration chamber and the heat exchange medium is performed sufficiently. To sufficiently perform this heat exchange, the specific surface area of the magnetic material must be increased. Setting a small particle size is effective in increasing the specific surface area of the magnetic

material of the present invention. However, if the particle size is too small, the pressure loss of the heat exchange medium increases. An optimum particle size must be chosen by taking this into account. The particle size of the magnetic material is preferably about 0.1 to 1.5 mm, and more preferably, about 0.2 to 0.8 mm.

Also, the particle shape of the magnetic material is preferably a smooth shape having no projection on the surface, e.g., a spherical shape or a spheroidal shape. By the use of a shape like this, it is possible to prevent the generation of fine particles caused by the crush of particles, and to suppress the increase in the pressure loss of the heat exchange medium.

For example, of the particles packed into the magnetic refrigeration chamber, 87 wt% or more of the particles preferably have a shape having an aspect ratio of 2 or less for the following reason. That is, the experiments were conducted by mixing odd-shaped particles having an aspect ratio of 2 or more into substantially spherical particles, the resultant particles were exposed to the flow of the heat exchange medium for a long time. In the case where the mixing amount of the odd-shaped particles was 13% or more, fine particles were produced, and the pressure loss of the fluid increased.

As the heat exchange medium, mineral oil, a

solvent, water, or a solution mixture of these

materials can be selected in accordance with the

operating temperature region of the heat cycle. As the

particle size of the magnetic material, an optimum

5    particle size is desirably selected within the

aforementioned range in accordance with the viscosity

(surface tension) of the heat exchange medium used and

the capability of the pump.

FIG. 8 shows an outline of the arrangement of a

10   magnetic refrigeration system using the magnetic

material based on the present invention. FIG. 9 shows

an outline of the arrangement of a heat exchange medium

circulating system of this magnetic refrigeration

system. Referring to FIGS. 8 and 9, reference numeral

15   1 denotes a magnetic material; 2, a magnetic

refrigeration chamber; 3, an inlet pipe; 4, an outlet

pipe; 5a and 5b, permanent magnets; 6a and 6b, rotation

tables; 25, a low temperature consumption site; and 26,

a radiator.

20   As shown in FIG. 8, the magnetic refrigeration

chamber 2 has a cylindrical shape with a rectangular

section. Mesh grids 11 and 12 are attached near the

two end portions of this magnetic refrigeration chamber

2. The magnetic material 1 based on the present

25   invention is packed between these mesh grids 11 and 12.

This magnetic material 1 consists of spherical

particles having an average diameter of 0.4 mm and is

packed with a volume packing ratio of 62% into the magnetic refrigeration chamber 2. The mesh size and Cu wire diameter of the mesh grids 11 and 12 are #80 and 0.14 mm, respectively. The heat exchange medium inlet

5    pipe 3 is connected to one end of the magnetic refrigeration chamber 2, and the heat exchange medium outlet pipe 4 is connected to the other end. In this embodiment, two magnetic refrigeration chambers 2 having the same shape are arranged parallel to each

10   other.

The pair of rotation tables 6a and 6b sandwich the two magnetic refrigeration chambers 2. These rotation tables 6a and 6b are supported by a common rotation axis 7. This rotation axis 7 is positioned in the

15   middle of the two magnetic refrigeration chambers 2. The permanent magnets 5a and 5b are held inside the circumferences of the rotation tables 6a and 6b, respectively. These permanent magnets 5a and 5b oppose each other and are connected via a yoke (not shown).

20   Accordingly, a strong magnetic field space is formed in the gap between these paired permanent magnets 5a and 5b. In this embodiment, two pairs of permanent magnets 5a and 5b are arranged, with the rotation axis 7 sandwiched in the middle, so as to correspond to the

25   two magnetic refrigeration chambers 2.

Whenever the rotation tables 6a and 6b are rotated 90°, the permanent magnets 5a and 5b repeatedly move

close to and away from the magnetic refrigeration
chamber 2. When each pair of permanent magnets 5a and
5b come closest to the side walls of the corresponding
magnetic refrigeration chamber 2, this magnetic

5      refrigeration chamber 2 is inside the magnetic field
space formed between these permanent magnets 5a and 5b.
So, the magnetic field is applied to the magnetic
material 1 contained in the magnetic refrigeration
chamber 2.

10      When the state in which the magnetic field is
applied to the magnetic material 1 switches to the
state in which the magnetic field is removed, the
entropy of the electron spin system increases, so the
entropy transfers between the lattice system and the

15     electron spin system. Consequently, the temperature of
the magnetic material 1 lowers, and this low
temperature is transmitted to the heat exchange medium
to lower its temperature. The heat exchange medium
whose temperature is thus lowered is discharged from

20     the magnetic refrigeration chamber 2 through the outlet
pipe 4 and supplied as a refrigerant to the low
temperature consumption site (25: FIG. 9) on the
outside.

As shown in FIG. 9, a storage tank 21 for storing

25     the heat exchange medium is installed on the upstream
side of the inlet pipe 3, and a pump 22 is placed
midway along the inlet pipe 3. The outlet pipe 4 is

divided into two piping systems after the magnetic
refrigeration chamber 2 to form circulating lines. A
valve V1, the low temperature consumption site 25, and
a valve V3 are arranged midway along one circulating

5    line (cooling line 23). The terminal end portion of
this cooling line 23 is connected to the storage tank
21. A valve V2, the radiator 26, and a valve V4 are
arranged midway along the other circulating line
(pre-cooling line 24). The terminal end portion of

10   this pre-cooling line 24 is connected to the storage
tank 21.

The operation of this magnetic refrigeration
system will be explained next. This magnetic
refrigeration system is operated by repeating a

15   pre-cooling process and a cooling process.

In the pre-cooling process, the valves V2 and V4
are opened with the valves V1 and V3 being closed,
thereby circulating the heat exchange medium in the
pre-cooling line 24. In this state, the permanent

20   magnets (5a and 5b: FIG. 8) are approached to the
magnetic refrigeration chamber 2. When the magnetic
field is applied to the magnetic material 1, the
temperature of the magnetic material 1 rises, and this
high temperature is transmitted to the heat exchange

25   medium to raise its temperature. The heat exchange
medium thus heated is discharged from the magnetic
refrigeration chamber 2 through the outlet pipe 4,

introduced to the radiator 26 through the valve V2, and

cooled in the radiator 26. The cooled heat exchange

medium is returned to the storage tank 21 through the

valve V4.

5    When the temperature of the magnetic material 1 in

the magnetic refrigeration chamber 2 lowers to the

vicinity of the temperature of the heat exchange medium

supplied to the magnetic refrigeration chamber 2

through the inlet pipe 3, the valves V2 and V4 are

10    closed to complete the pre-cooling process, and the

cooling process is started.

In this cooling process, the permanent magnets (5a

and 5b: FIG. 8) are moved away from the magnetic

refrigeration chamber 2. The valves V1 and V3 are then

15    opened to circulate the heat exchange medium in the

cooling line 23. When the magnetic field is removed

from the magnetic material 1, the temperature of this

magnetic material 1 lowers, and this low temperature is

transmitted to the heat exchange medium to lower its

20    temperature. The heat exchange medium thus cooled is

discharged from the magnetic refrigeration chamber 2

through the outlet pipe 4, and supplied to the low

temperature consumption site 25 through the valve V1.

After the temperature of the heat exchange medium is

25    raised as it is used in this low temperature

consumption site 25, the heat exchange medium returns

to the storage tank 21 through the valve V3.

When the temperature of the magnetic material 1 in
the magnetic refrigeration chamber 2 rises to the
vicinity of the temperature of the heat exchange medium
supplied to the magnetic refrigeration chamber 2

5 through the inlet pipe 3, the valves V1 and V3 are
closed to complete the cooling process, and the
pre-cooling process is started again.

A controller (not shown) of this magnetic
refrigeration system controls the valves V1 to V4 in

10 synchronism with the movement of the permanent magnets
5a and 5b, thereby alternately repeating the
pre-cooling processing and the cooling process
described above.

15 When the magnetic material of the present
invention is used in near room temperature region, an
inflection point appears on the magnetization curve
with a relatively low magnetic field. In addition,
near the temperature at which this inflection point

20 appears on the magnetization curve, a large entropy
change is observed in the electron spin system.
Accordingly, when this magnetic material of the present
invention is used, magnetic refrigeration can be
realized using a relatively low magnetic field by

25 exchanging the entropy between the electron spin system
and the lattice system near the above-mentioned
temperature.

Also, by combining this magnetic material and
permanent magnets, a small, simple, inexpensive
magnetic refrigeration system can be configured without
using any superconducting magnet.

5       Additional advantages and modifications will
readily occur to those skilled in the art. Therefore,
the invention in its broader aspects is not limited to
the specific details and representative embodiments
shown and described herein. Accordingly, various

10    modifications may be made without departing from the
spirit and scope of the general inventive concept as
defined by the appended claims and their equivalents.